

Nuclear Spin

To explain nuclear and electronic *spin* we need to revisit the earliest discoveries of electricity and magnetism.



Hans Christian Ørsted (pictured left) was a Danish scientist who discovered that electric currents create magnetic fields. He found that if two wires carry an electric current, which we now know to be the movement of electrons, in the same direction then they attract each other and the wires are pulled slightly towards each other. On the other hand if the wires contain electric currents travelling in opposite directions the wires repel each other and move slightly apart from each other. Ørsted demonstrated that this attraction and repulsion was due to magnetism by placing a small compass in multiple positions adjacent to the current – carrying wires and recording the deflections of the needle. He thus became the first person to connect electricity and magnetism and this led to the concept of electric and magnetic fields which, in turn, led to the determination, mathematically by James Clerk Maxwell, that electromagnetic radiation was created by a combination of the two fields. The key point for us is that a moving charge generates a magnetic field.

The converse must also be true i.e. a magnetic field can make a charged particle move simply because there is no reason for that not to occur. In this context movement does not necessarily mean physical movement from one position to another. It can simply mean the particle is rotating on its axis. Ørsted's discovery revealed a fundamental connection between charged particles which can, mathematically be considered as an electrical field and a magnetic field. Both the electron and the nucleus are moving charges since they rotate i.e. spin. As with a child's spinning top, the electron can spin in a clockwise or an anti-clockwise direction. The spinning electron charge generates a magnetic field since it is moving i.e. rotating. It does not have to change physical location to be moving. If one electron spins in a clockwise direction it will generate a magnetic field in an upwards direction. Likewise, an electron spinning in an anti-clockwise direction will generate a magnetic field in the opposite direction. The two opposing magnetic fields will repel each other but the repulsion is overcome by the attractive power of the nucleus so they are forced to remain in the orbital.

This principle though does explain why no orbital can contain more than two electrons.

In a filled orbital i.e. one containing two electrons, the electrons spinning in opposite directions will generate opposing magnetic fields but be kept in place. On the other hand, a third electron, also spinning, will generate a magnetic field in one direction or another and will be repelled by one of the two electrons. This explains why an orbital can only contain a maximum of two electrons.

Just as with electrons, a spinning nucleus generates a magnetic field. If we consider the ^1H nucleus, it is simply a proton and can spin in a clockwise or an anti-clockwise direction. In the absence of an applied, external magnetic field, on average, 50% of the hydrogen nuclei will spin in one direction and 50% in the opposite direction.

Under certain circumstances the spinning nucleus can be made to change its spin from clockwise to anti-clockwise and vice versa and is explained later as this principle forms the basis of nuclear magnetic resonance and is discussed below.

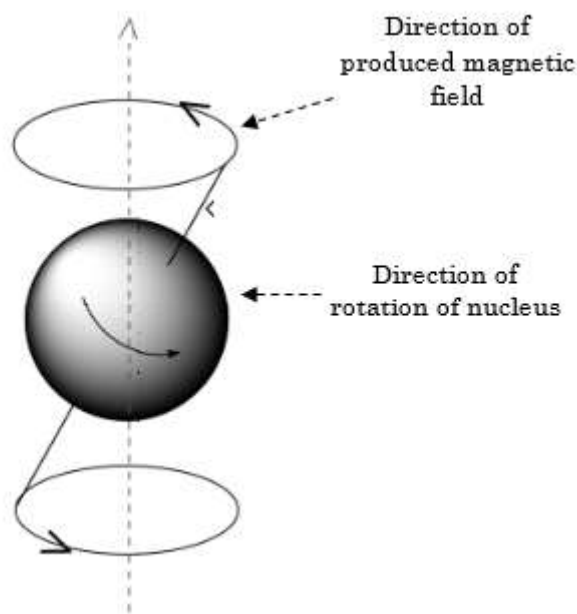
If we picture the atom to comprise a small dense, positively charged nucleus surrounded by electrons then we can envisage the nucleus rotating in a clockwise direction or an anti-clockwise direction. The electrons will also be spinning on their axes but their analysis is an entirely different discipline, *Electron Spin Resonance Spectroscopy*, which is not relevant for the purposes of these volumes.

We know that a moving charge generates a magnetic field and rotation of a positive charge is as much movement as is physical translation from one physical location to another.

The magnetic fields generated will point in opposite directions. Since the nucleus rotates at a slight angle the magnetic field described by the rotating nucleus is a circle. This is analogous to the rotation of the Earth where magnetic North is not literally at the top of the planet.

This process is known as *precessing* and is best considered visually as demonstrated on the right.

For mathematical reasons, the spin of the nucleus is denoted as either $+\frac{1}{2}$ or $-\frac{1}{2}$, abbreviated to $\pm\frac{1}{2}$. Given that the magnetic field can point up or down the rotation of the nucleus is described as *spinning up* or *spinning down*. For even greater simplicity, the entire atom can be described symbolically simply as an up arrow or a down arrow. In the absence of a strong magnetic field (that of the Earth is too weak to be of any effect) the atoms are all of a jumble and will precess in all 360° directions and can be represented in the following manner, with each arrow indicating the direction of the magnetic field of an atom.

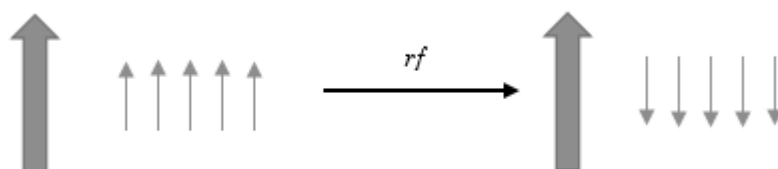


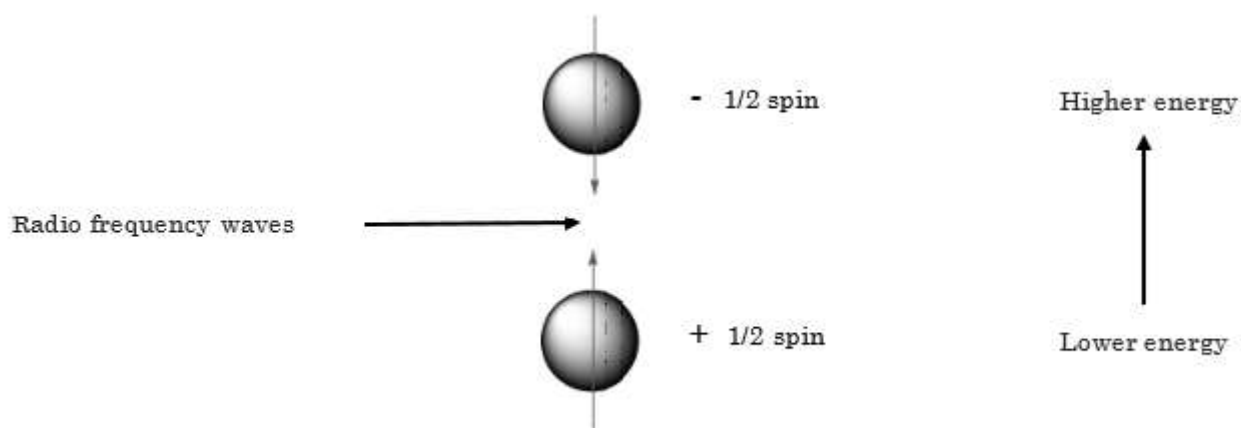
In the presence of a strong magnetic field, however, all the atoms can be made to orient in the same direction and, where B is the strength of the applied magnetic field, can be represented as follows:



This is the lower, $+\frac{1}{2}$, energy state of the atoms and it was theorised that if the aligned atoms were irradiated with radiowave frequencies (rf) the atoms could all be made to flip from the lower energy ($+\frac{1}{2}$) orientation to the, higher, $-\frac{1}{2}$, spin state:

This transition can also be represented as shown below:





To achieve this the magnet has to be extremely powerful, many hundreds of thousands of times more powerful than the Earth's magnetic field, but a fortunate consequence of this is that the frequency of the radiowave radiation required to flip the nucleus is in the radiowave region of the electromagnetic spectrum, specifically UHF (TV) and VHF (radio).

This idea was first conceived, in 1936, by the Dutch physicist Cornelis Gorter but he could not secure the finances necessary to build the required equipment. His concept was demonstrated one year later by Isidor Rabi (Nobel Laureate, 1944). Rabi established the principle by demonstrating that a stream of lithium ions could be flipped from the lower to the higher energy state.

The next significant development was made by Felix Bloch and Edward Purcell who independently, and almost simultaneously, demonstrated the phenomenon using paraffin wax and water respectively. They were the joint Nobel Physics Laureates for this discovery in 1952.

The huge number of Nobel Prizes awarded for this research demonstrates that the potential of nuclear magnetic resonance has never been underestimated.

This was swiftly followed by the discovery that different hydrogen atoms attached to different carbon atoms, generating specific magnetic fields could be flipped, and be detected and identified individually.

In each circumstance, the specific radio frequency is unique to that specific environment and meant that each individual chemical and magnetic environment could be differentiated by measuring the specific frequency at which these flips occur. A further conclusion was that the measurements also indicated the relative number of hydrogens of each type.

A question often asked is why certain nuclei demonstrate this phenomenon and others do not. For example, the ^1H isotope does resonate with the magnetic field but the ^2H isotope does not. With regard to carbon, ^{12}C does not but ^{13}C does.

The reason for this is straightforward.

The *nucleons*, neutrons and protons, all spin within the spinning nucleus. If the number of nucleons is an even numbered integer then the spins of these nucleons cancel each other out and the nucleus does not experience any effect of the magnetic field.

For example,

- The ^{12}C isotope contains 6 protons and 6 neutrons and so does not resonate. The ^{13}C isotope has the same number of protons (6) but 7 neutrons and so has an odd number of nucleons and does resonate.
- ^1H has one proton and no neutron so resonates whilst ^2H has one proton and one neutron and does not.

The lack of resonance of the ^2H and ^{12}C has both advantages and disadvantages:

- The ^1H isotope comprises 99.98% of all hydrogen atoms whilst ^2H comprises a mere 0.2%. This means that the ^1H nmr measurement provides a very clear, detailed and strong spectrum in a matter of minutes.

Although analysis of solid samples is possible, for organic compounds, all nmr measurements are conducted on a sample dissolved in a suitable solvent.

Most organic compounds dissolve in either water or a solvent such as chloroform. If dissolved in ordinary water or chloroform then nothing would be detected in the nmr experiment since the ^1H isotopes present would completely swamp the signal from the sample since the solvent molecules are present in many trillions of times in excess of the sample molecule.

That the ^2H isotope does not resonate means that, if the compound is water – soluble then it can be dissolved in $^2\text{H}_2\text{O}$, also known as heavy water (D_2O), whilst those soluble in organic solvents can be dissolved in deuterated chloroform C^2HCl_3 , also and less clumsily written as CDCl_3 .

Note that, traditionally, many chemists have referred to ^2H as deuterium but the use of specific names and symbols for ^2H (deuterium) and ^3H (tritium) is now discouraged since there is no rationale for the three isotopes of hydrogen to have different names whilst no isotopes of any other element do. There are, however, times when it is more convenient to use those symbols and chemists use whichever is simplest even if it is inconsistent with stated principles hence the common use of CDCl_3 and D_2O .

- The most common carbon isotope (^{12}C) which comprises approximately 99% of all carbon atoms does not contribute to the nmr spectrum whilst ^{13}C does. Since ^{13}C comprises only 1% of all carbon atoms, the ^{13}C nmr spectrum takes many hours to collect and is still very noisy.

The lack of resonance of the ^{12}C isotope does, however, confer its own advantage.

Typically, the spectral range is from 0 – 220 ppm (discussed below) and the distinct chemical and magnetic environments enable rapid differentiation of, and distinguishing between, different environments.

Moreover the tiny proportion of ^{13}C isotopes means that it is highly unlikely that two such isotopes will be present in the same molecule to any great extent and this means that their magnetic fields do not interfere with each other and so there are no doublets, triplets etc; as discussed below.

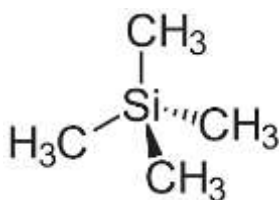
Chemical Shift

A note about the units of the spectra.

The strength of the magnet is fixed and, consequently, all measurements are of the frequencies of the radio waves that are absorbed. NMR spectrometers operate at different frequencies. Those producing low resolution spectra typically operate at 90MHz with relatively low strength magnets whilst high resolution machines operate at 200MHz, 300MHz, 360MHz, 400MHz and 500MHz. The magnets involved are huge in order to produce the fields needed and however high the quality of the manufacturing it is impossible to ensure that they are all consistently manufactured. The slightest difference in the magnet can vary the magnetic field sufficient to produce shifts at different frequencies.

The solution is to measure the frequencies relative to a known standard material.

The standard used is tetramethylsilane (TMS) which has the formula $\text{Si}(\text{CH}_3)_4$. This produces a very strong signal due to the presence of 12 hydrogen atoms per molecule and since the molecule is tetrahedral all the hydrogen atoms are both *chemically* and *magnetically* equivalent so produce a sharp singlet.



The molecule is tetrahedral and, in a two dimensional diagram, the hatched line represents a group behind the page whilst the broad arrow points in from the front of the page.

All measurements are converted into the *chemical shift* (δ) using the formula for each peak:

$$\text{Chemical shift } \delta = \frac{\text{frequency of signal} - \text{frequency of TMS}}{\text{Spectrometer frequency}} \times 10^6$$

Since, in this case the frequency of the signal is equal to the frequency of TMS, the numerator is zero which means that whatever the frequency or the strength of the magnet, TMS always appears as zero and all other measurements are calculated relative to the $\delta 0$ ppm (parts per million).

The multiplication by 10^6 is simply to ensure the numbers are manageable since the frequencies are in the Megahertz (MHz) range.

The use of the units, whilst correct, is often neglected again for simplicity with the assumption that all those analysing the spectra understand that the chemical shift does have units.

The *chemical shift* has a number of advantages.

Firstly it takes account of manufacturing differences, as explained before, but for a chemist interpreting a spectrum the range of δ values, 0 – 12 ppm for ^1H spectra and 0 – 220 ppm for ^{13}C spectra, is much easier than considering huge frequencies which few people can grasp, appreciate and compare.

It should also be noted that, although ^1H and ^{13}C measurements are by far the most commonly performed nmr spectroscopic measurements, other nuclei including ^{10}B , ^{11}B , ^{14}N , ^{17}O , ^{19}F and ^{31}P do resonate but are much less common and are not considered in the other two volumes of this series.

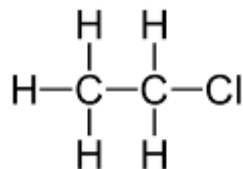
The most effective way to learn to interpret spectra is to analyse some and this is what we will now do, starting with ^1H and then continuing with ^{13}C nmr spectra.

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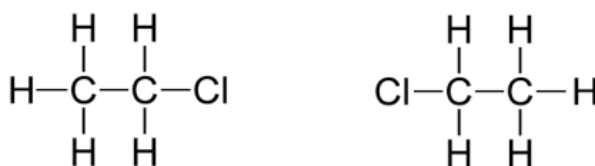
^1H NMR spectroscopy

Chemical and magnetic equivalence

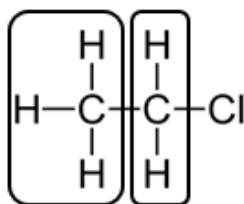
We will consider *chloroethane* ($\text{CH}_3\text{CH}_2\text{Cl}$)



which can only exist in the one form since the structures displayed below are identical as one can be turned over to appear the same as the other i.e. they are mirror images and are identical.



It is, however, clear that there are two different types of hydrogen atoms as indicated below:



Given that these hydrogen atom groups experience different magnetic fields they can be distinguished since they will resonate at different frequencies.

1. The ^1H nmr spectrum will therefore, as a first step, comprise two peaks due to the:-

- – CH_3 group
- – CH_2 group

The position of these peaks are stated as chemical shifts which is a concept discussed below.

2. Secondly since the intensity of the resonant signal is proportional to the number of hydrogen atoms, the areas under the peak will be in the ratio of 3:2. The measurements of the areas (known as the *integrals*) are not absolute and are relative to each other.

This means that we can now expect the spectrum to comprise two peaks with one of 50% area greater than the other. This immediately indicates which peak is due to the – CH_3 group (the larger peak by area) and which is caused by the – CH_2 group (the smaller peak again by area).

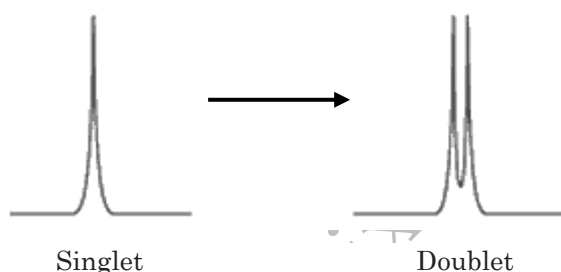
However there is one further great benefit to the ^1H nmr experiment and that is due to interactions between the magnetic fields of hydrogen atoms on adjacent carbon atoms, the ***n+1 rule***.

Peak Multiplicity

The ***n+1 rule*** states that a single peak will be split by the number of hydrogen atoms on adjacent hydrogens. This is due to the atoms either spinning up or spinning down.

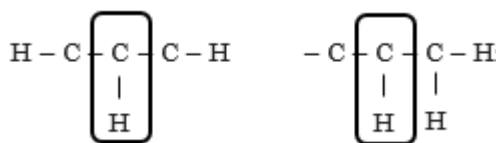
If we consider a single hydrogen atom then if there were no adjacent hydrogens the hydrogen will produce a single peak. However, if there is one hydrogen atom on one of the immediately adjacent carbon atoms, that hydrogen atom may itself be spinning up or down. These create slightly different magnetic environments. Within the entirety of the sample then, on average, there will be equal number of hydrogens spinning up and spinning down. Although *chemically equivalent*, these hydrogen atoms are **not magnetically equivalent** and will resonate at slightly different frequencies.

Consequently a lonely hydrogen atom's single peak, a *singlet*, is split into two peaks of equal height which is known as a *doublet*.

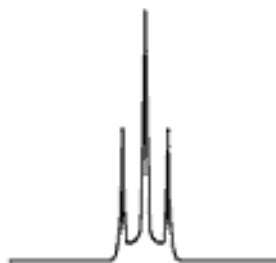


The area under the doublet, the *integral*, is equal to the area under the singlet.

The same principle applies to a hydrogen atom (highlighted) with two hydrogen atoms on adjacent carbons. It makes no difference if the hydrogens are all on one of the immediately adjacent carbon atoms or are distributed across both i.e. both scenarios produce a triplet since both there are two hydrogens on adjacent carbon atoms.



This means that both of these situations will produce a triplet.

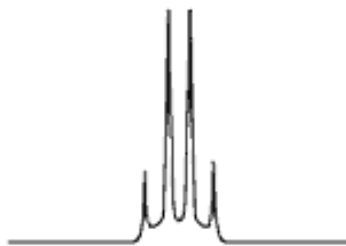


as, in both cases, the analysed hydrogen has two hydrogen atoms on immediately adjacent carbon atoms.

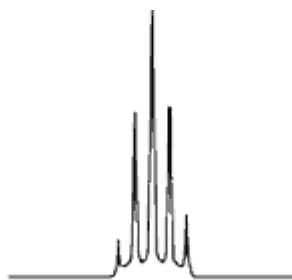
As above the area under the triplet equals that of the area of what would have been a singlet.

The process continues with a singlet split into a:

- **quartet** when there are **three** hydrogens on the immediately adjacent carbon atoms:



- **quintet** when there are **four** hydrogens on the immediately adjacent carbon atoms:



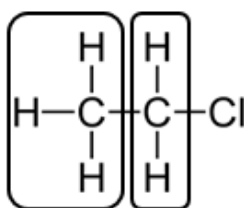
The doublets, triplets, quartets etc; are collectively referred to as *multiplets*.

In sum, the number of hydrogens splits the singlet into a peak with the *number of adjacent hydrogens +1*.

This is the ***n+1 rule***.

This rule immediately identifies how many hydrogen atoms are on immediately adjacent carbon atoms which also demonstrates that the effects do not exist beyond two bonds.

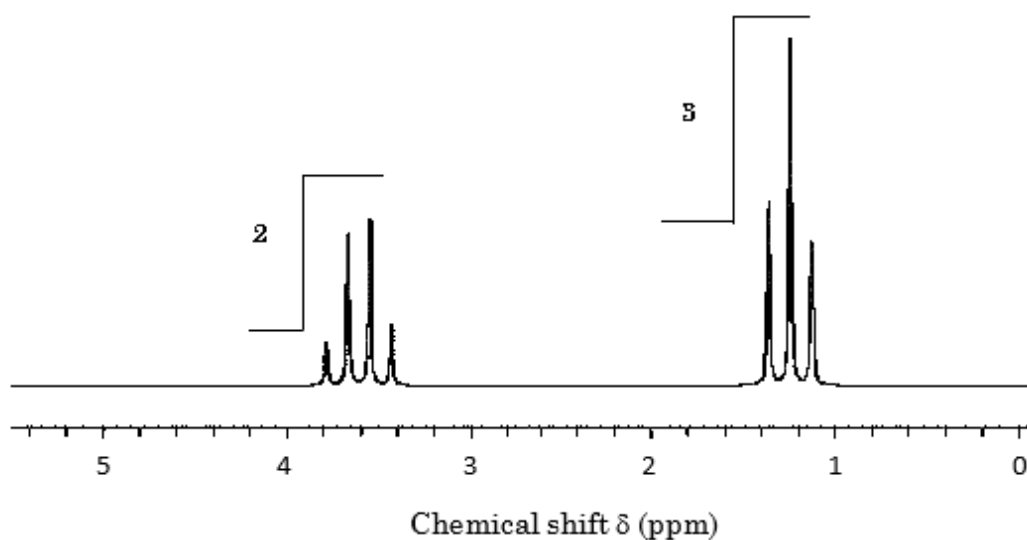
If we reconsider the highlighted structure of the molecule,



we may now conclude that there are:-

- **Two** types of chemically and magnetically equivalent hydrogen atoms and so **two groups of peaks**.
- If we consider the – CH₃ group, then the peak of relative area **3**, must be a *triplet* as there are two hydrogen atoms on the adjacent carbon.
- With regard to the – CH₂ group, then the peak of relative area **2**, must be a *quartet* as there are three hydrogen atoms on the adjacent carbon.

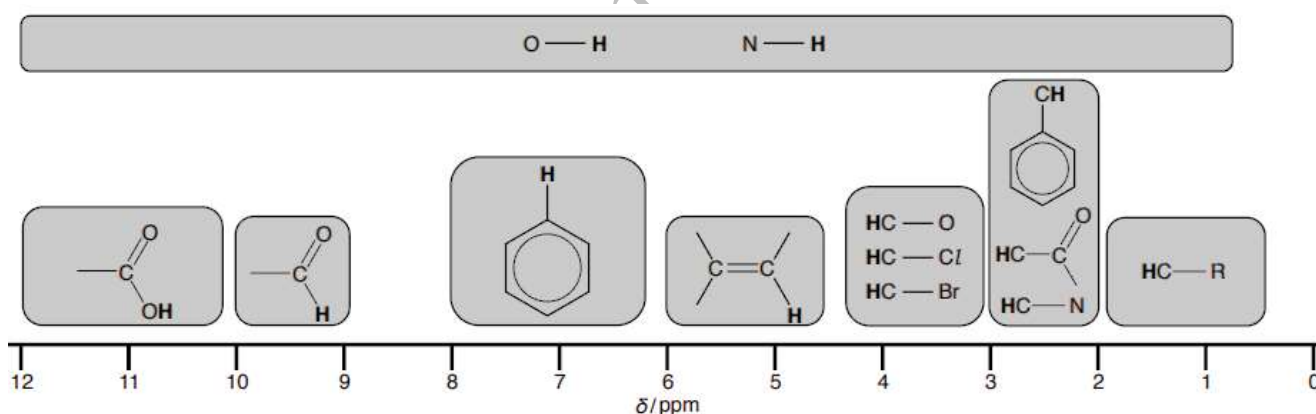
Essentially, therefore, the ^1H nmr spectrum will comprise these two groups. When we perform the actual measurement we obtain the following spectrum:



It is, therefore, perfectly clear which multiplet is produced by each set of C – H atoms.

The spectrum of chloroethane demonstrates the power of the ^1H nmr spectroscopic technique. The other real power is that the different types of hydrogen atoms can be identified using a correlation chart since they appear, consistently for a huge range of compounds in the same region.

A useful example is shown below:-

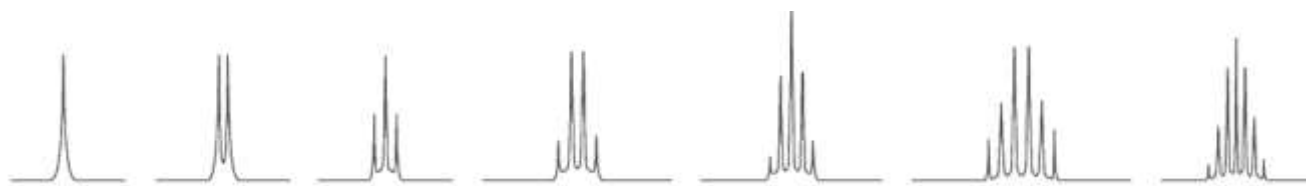


The only difficulty arises from the labile O – H and N – H hydrogen atoms since they can appear almost anywhere in the spectrum.

There are other matters to note about the spectra which are not necessary for the interpretation of spectra in the following two volumes of this series but are extremely interesting.

Peak heights in a multiplet

If we consider the patterns and shapes of a multiplet, from a singlet to a septet,



It becomes clear that within the multiplet there is a definite and clear pattern in the peaks:

Multiplet	Number of peaks	Ratio of peak heights
Singlet	1	1
Doublet	2	1:1
Triplet	3	1:2:1
Quartet	4	1:3:3:1
Quintet	5	1:4:6:4:1
Sextet	6	1:5:10:10:5:1
Septet	7	1:6:15:20:15:6:1

The ratio of peak heights is the pattern of integers famous in the Western world as Pascal's Triangle. This pattern has been known for at least 1,000 years though; in Iran it is known as the Khayyam Triangle whilst in China it is called Yang Hui's Triangle.

Blaise Pascal (1623 – 1662) became famous for his book describing a huge number of applications in business, pure mathematics and probability and his name became attached to the triangle even though it had been known for hundreds of years. Pascal was also renowned for his work on vacuums and on pressure and the unit of pressure, mathematically Newtons per square metre, N/m^2 , is termed the Pascal (Pa) in his honour. He is also credited with being one of the first inventors of the mechanical calculator.

Even though Pascal cannot possibly have considered the application in a technique of which he had no conception it is extremely useful in predicting the multiplet peaks in complex molecules. When we have a molecule with a number of distinct but similar groups the peaks, although being chemically and magnetically equivalent, will appear in the same region of the 1H nmr spectrum and often overlap. Knowing the ratios of the peak heights allow us to separate out the multiplets and assign them appropriately.

For example, all alkane hydrogen atoms appear between δ 0.5 and δ 1.9 ppm. With a large molecule there will be a significant number of peaks in that region and the multiplet peak heights enables them to be distinguished.

There is another aspect to the multiplets and that is the distance between the peaks in a multiplet.

This is due to a phenomenon known as the *coupling constant* which is discussed next.

Coupling Constants

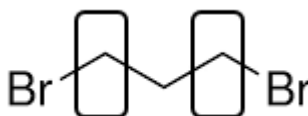
When protons communicate with each other the effect exerted by one on another must be reciprocated. This is measured by calculating the distance between the peaks of a multiplet. Two groups of protons on nearby carbon atoms will have the same *coupling constant*, referred to as J , and which is measured in Hertz (Hz).

If they do not have the same coupling constant then they are not communicating and hence **not** adjacent.

If we consider 1,3 – dibromopropane



Since the molecule is symmetrical around the central – CH₂ group, We can immediately see that there are two sets of chemical and magnetically equivalent groups:



These are identical to each other but different to the central – CH₂ group which is circled:

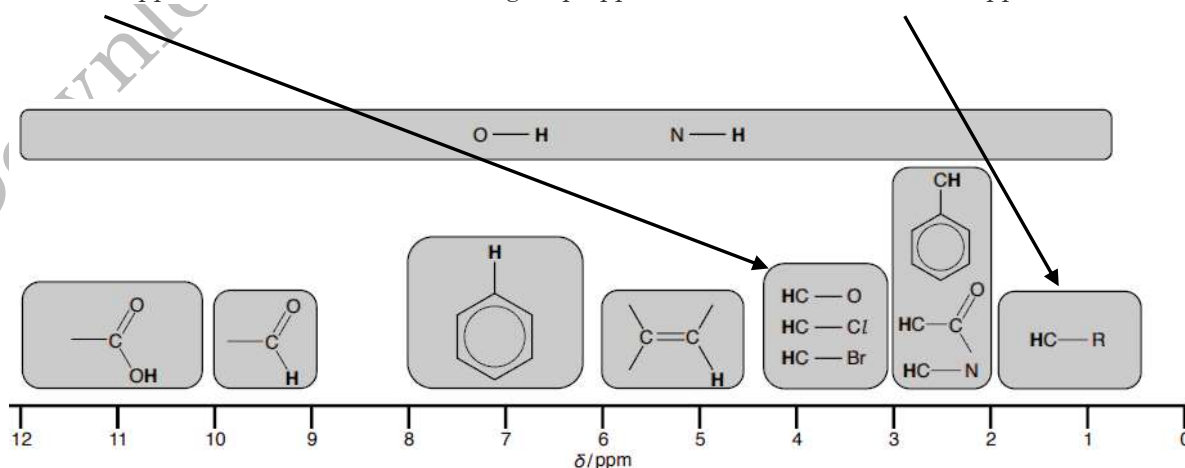


The structural formula and the molecular formula BrCH₂CH₂CH₂Br enables us to predict that there will be two multiplets in the ¹H nmr spectrum in the ratio 2:1.

- One group will be due to the hydrogens on the terminal carbons of which there are four.
- The second group will be due to the central, circled, hydrogens of which there are two.

Since we use the smallest whole number ratio the areas under the groups will be in the ratio 2:1

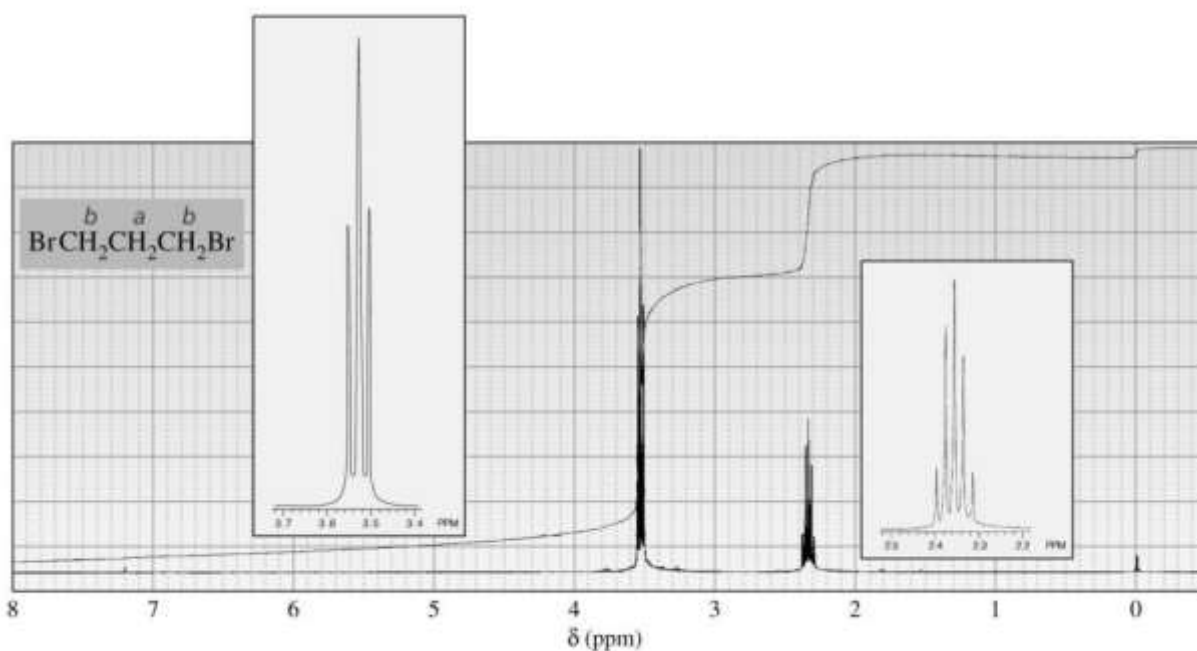
Referring to the correlation table, we can see that the hydrogens on the terminal carbons will appear between δ 3 ppm and δ 4.3 ppm whilst the central – CH₂ group appears between δ 0.5 and δ 1.9 ppm



As well as this, with our knowledge of the $n+1$ rule, we can, also predict that since

- the central $-\text{CH}_2$ group has a total of four hydrogen atoms on adjacent carbon atoms, this will produce a quintet and with our knowledge of chemical shifts, this will appear between δ 3 and δ 4 ppm.
- The terminal $-\text{CH}_2(\text{Br})$ peak will generate a triplet since both ends of the molecule are identical and each of the hydrogen atoms on the group have two hydrogens on the central carbon atom and will be somewhere around δ 2 ppm. Due to the presence of the electronegative bromine atoms, it will be deshielded and will appear to the extreme left of the alkyl region of the correlation chart.

The actual ^1H nmr spectrum is as shown below:



The multiplet peak shapes are as predicted but the $-\text{CH}_2\text{Br}$ group is slightly to the left of the region identified in the correlation chart which shows both its use and its limitations. The one used in this volume is suitable for the compounds analysed in Volumes II and III of this series and has been selected for its simplicity. More detailed correlation charts would have predicted this shift but can be overly complicated at one and the same time. No correlation chart can cover all scenarios unless we want a very busy chart which would be difficult to navigate.

What is really interesting from our perspective though is the coupling constants of the two multiplets. They are significantly different, indicating that the protons on the terminal carbons do not communicate with those on the central $-\text{CH}_2-$ hydrogens.

Without going into huge detail, analysis of numerous compounds have produced a number of general rules and two examples stand out.

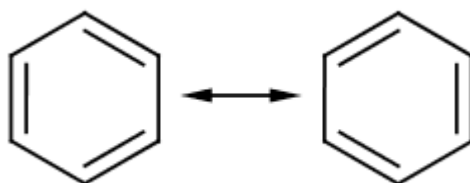
One group that has not been addressed yet are aromatic rings such as benzene and substituted benzene molecules.

The second group comprises the cis- and trans- isomers of alkenes.

Both of these groups inform us of their structures through the chemical shift and the coupling constant.

The ^1H nmr spectroscopy of benzene

Benzene is famous for its stability which can be drawn as two, Kekulé, structures:-



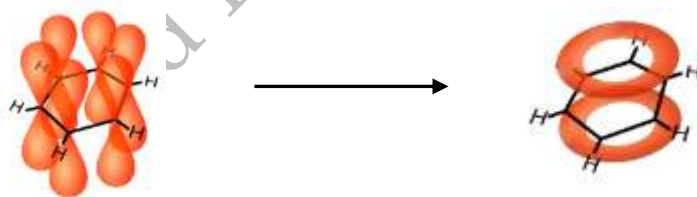
where the double headed arrow represents two possible and equivalent structures

This, however, cannot be correct for four reasons:

- The benzene molecule would react with three mole equivalents of bromine water which it does not
- There should be two types of chemically and magnetically equivalent hydrogen atoms so the ^1H nmr spectrum should show two peaks of equal integral. This is not what occurs and the spectrum contains only one peak at $\delta 7.35$ ppm.
- Equally significantly, this peak is significantly downfield of the alkene region which is typically from $\delta 4.5 - 6.5$ ppm
- From our knowledge of bond lengths, would have three long C – C and three shorter C = C bonds. In fact all the C – C bond lengths in the ring are the same length and are intermediate between the lengths of the single and double carbon – carbon bond lengths.

The reason for this is the overlapping of the p – orbitals creating a delocalised orbital containing six electrons, one from each of the constituent carbon atoms.

The six p – orbitals overlap (below left) creating a ring above and beneath the planar carbon skeleton in which the six p – electrons travel around the ring (below right)



This leads to all the carbon – carbon being equivalent and explains why they are all the same length in what become so called *aromatic* compounds. This also means that, in benzene, all the hydrogen atoms are chemically and magnetically equivalent and the benzene ring is drawn as:

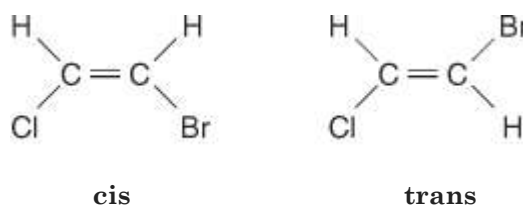


All so called aromatic compounds resonate in the region $\delta 7 - \delta 8$ and this means that any peak present there can be immediately be assigned to the presence of an aromatic ring. This is important when we consider the structure of benzaldehyde, the natural almond flavouring, in Volume III of this series.

The other interesting situation, from our perspective is the isomerism of alkenes which we consider next.

The ^1H nmr spectroscopy of isomers

We can take bromochloroethene as an example. Since the $\text{C}=\text{C}$ bond is rigid, due to overlap of the p – orbitals, there are two possible structures:



Cis and trans are old terminologies (*cis* = together i.e. on the same side whilst *trans* = across i.e. on opposite sides of the $\text{C}=\text{C}$ which have been pretty much replaced by (E) – and (Z) – terms but they are still used.

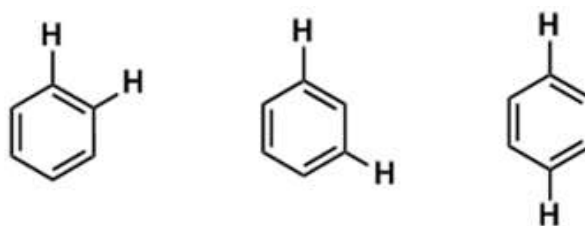
Using our knowledge of spectroscopy and spectrometry, we can immediately determine that:-

- The infrared spectrum would identify the presence of the $\text{C}=\text{C}$ and $\text{C}-\text{C}$ bonds (in the fingerprint region) with, of course, the useless $\text{C}-\text{H}$ stretches present in all organic molecules. In addition, there will be $\text{C}-\text{Cl}$ and $\text{C}-\text{Br}$ peaks in both spectra so that doesn't help.
- The mass spectrum would produce the same fragmentation patterns for both so that doesn't help.
- Superficially, the ^1H nmr spectra would appear the same with the same peaks with the same chemical shifts since each hydrogen is attached to a carbon atom bonded to a halogen but here comes the difference: the coupling constants in the spectra are found to be different.

Naturally the ^1H nmr spectra of the two isomers will be similar but it is found that the coupling constants of cis – and trans – isomers are different. It's a small difference but is nevertheless highly significant. The coupling constant, J , (the distance between the peaks of a multiplet) is smaller for cis – isomers than for trans – isomers and typically the differences are as shown below:

Isomer	J (Hz)
Cis	6 – 15
Trans	11 – 18

There is clearly some overlap but it is clear that any J value below 11Hz indicates that the molecule possesses a cis – structure whilst anything above 15Hz demonstrates that the isomer must be trans. Reverting to aromatic compounds, we can consider the three possible isomers of substituted benzenes. Nowadays we number the arrangements but they are traditionally known as ortho – , meta – and para – as shown below:



Coupling constants: Ortho: 7 – 10 Hz Meta: 2 – 3 Hz Para: 0 – 1 Hz

It is clear that we can use the coupling constant, J , to distinguish between the isomers of a substituted aromatic ring.

To sum up then, with ^1H nmr spectra we can identify the position and numbers of individual hydrogen atoms in a molecule by way of:-

- Chemical shift δ ppm;
- Area under the peak, the integral;
- Multiplicity of the signal;
- The coupling constant, J .

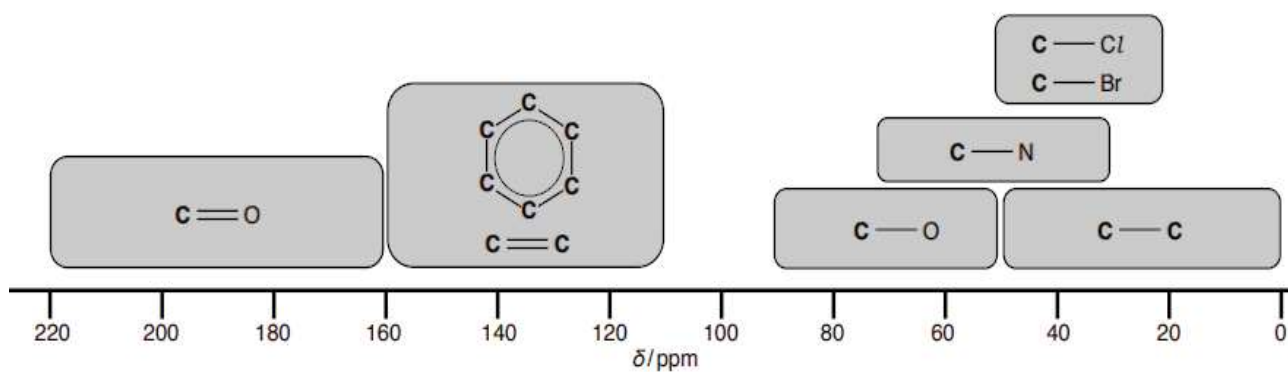
That may appear to be everything we can learn about the structure of a molecule but that is before we consider the application of ^{13}C nmr spectroscopy which is discussed next and is thankfully much simpler than ^1H nmr spectroscopy!

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^{13}C NMR spectroscopy

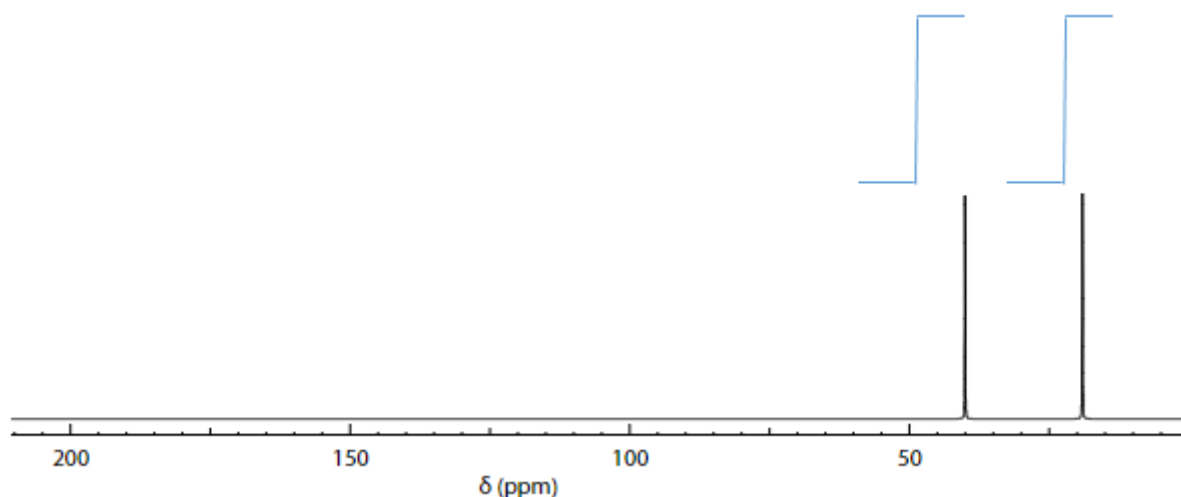
The interpretation of a ^{13}C nmr spectrum is, in many ways, simpler than the ^1H spectrum for the simple reason that the predominant ^{12}C isotope (99% of all carbon atoms) does not resonate with the electromagnetic spectrum and so the measurement is of the ^{13}C isotope only. The reason for this is explained above.

As also discussed above, given its relatively rare occurrence, it is highly unlikely that two such isotopes will exist in the same molecule so there will be no couplings between the atoms and the peaks in a ^{13}C nmr spectrum are only ever singlets. That might appear a disadvantage but this is overcome by the range of chemical shifts in such a spectrum as shown below:



There is therefore rarely much difficulty in assigning the peaks to specific carbon atoms in small molecules.

If we refer to chloroethane again we can predict that there will be two peaks of equal area and this is indeed what we observe:



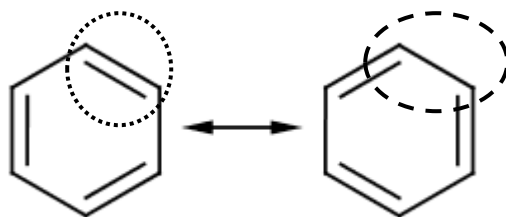
From the correlation chart we can conclude that the peak at $\delta 40$ ppm is due to the chlorine substituted carbon, $-\text{CH}_2\text{Cl}$, whilst the peak at $\delta 19$ ppm is due to the alkane carbon, $-\text{CH}_3$.

Although the regions overlap the $\text{C}-\text{Cl}$ carbon does not appear below $\delta 20$ ppm so it is straightforward to distinguish between the groups.

There is no coupling due to the unlikelihood of two ^{13}C isotopes co-existing adjacently but the area under the peak, the integral, applies just as it does in the ^1H nmr spectra.

The ^{13}C nmr spectroscopy of benzene

If we reconsider the Kekulé structures of benzene,



we can see that there are two types of carbon atom,

- three that are doubly bonded C = C, circled with a dotted line (above left) and
- three which are singly bonded, C – C, identified by the oval with a dashed arrow (above right).

If the above structure is correct then we should observe two peaks of equal integral, one in the region δ 115 – 160 ppm, assignable to a C=C bond, and one in the region 0 – 50 ppm due to the presence of the C – C bond.

That is not what we observe and the ^{13}C nmr spectrum comprises one peak, a singlet, at δ 144.5 ppm.

We have now explored the principles, application and power of spectroscopic and spectrometric analytical techniques and practical examples are exemplified, for small molecules, in Volume II and natural flavourings in Volume III. In both handbooks, the first few examples are worked through in full with the remainder to practice on, with full answers at the end of each handbook.

The following chapter records, as pen portraits, the lives and achievements of the scientists and engineers who completely changed our view of the world.